



ontario hydro research division

TO: Mr. F.J. Kee
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**POSTER PRESENTATION AT THE CONFERENCE ON
LASERS AND ELECTRO-OPTICS MAY 23, 1985**

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The Conference on Lasers and Electro-Optics is the largest annual technical meeting of laser scientists from around the world. In one of the poster sessions we presented results obtained recently in Ontario Hydro Research Division on assessing a new wavelength region for laser isotope separation of tritium. Absorption measurements in trifluoromethane have demonstrated greater selectivity for CF_3T from CF_3H and CF_3D at $5.2 \mu\text{m}$ than at $9.3 \mu\text{m}$. Theoretical calculations predict that tritium separation from both protium and deuterium is economically reasonable at $5.2 \mu\text{m}$ if the physics of dissociation is similar to that at $9.3 \mu\text{m}$. Experiments to demonstrate multiphoton dissociation at $5.2 \mu\text{m}$ are being planned.

INTRODUCTION

The Conference on Lasers and Electro-Optics is held annually in North America as a forum for discussion and exhibition of recent developments in lasers and laser applications. Over 4000 people attended the conference, located this year in Baltimore, Maryland, May 21-24. A more detailed account of the papers presented and information obtained is included in another report /1/. As part of this conference a poster paper was presented based on work carried out over the last few months at Ontario Hydro Research Division and partially funded by the Canadian Fusion Fuels Technology Project. The ongoing work consists of experiments to assess the potential of a new wavelength region for laser isotope separation of tritium by multiphoton dissociation of trifluoromethane. The results described in the paper show that selective absorption by CF_3T in mixtures of CF_3H and CF_3D is greater at the new wavelength, $5.2 \mu\text{m}$, than at the old wavelength, $9.3 \mu\text{m}$. The results are sufficiently encouraging that we should proceed with experiments on multiphoton dissociation of CF_3T at $5.2 \mu\text{m}$, and thus complete the assessment for laser tritium separation at this wavelength. A full description of the poster paper is attached as Appendix A, which is a copy of the handout distributed on request to conference attendees. This report provides a summary of that paper and includes a discussion of future work.

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SUMMARY OF PRESENTATION

The first step in assessing a particular infrared wavelength for laser isotope separation is to measure the selectivity of the optical absorption for the chosen isotopic molecule from the other molecules. The second step requires a demonstration of multiphoton dissociation. The poster presentation examined the first step in detail for CF_3T near $5.2\text{ }\mu\text{m}$, which is one of the two regions of strong absorption in this molecule that are accessible by high power lasers. The experiment employed a frequency-doubled CO_2 laser that was built expressly for generating pulsed laser energy tunable over a wide range around $5.2\text{ }\mu\text{m}$. With this light source and conventional techniques we measured cross-sections for optical absorption in CF_3H and CF_3D . The selectivity for CF_3T was calculated by taking the ratio of published absorption cross-sections for CF_3T to our measured values for CF_3H and CF_3D . We did not measure the absorption in CF_3T in our laser laboratory because the high specific radioactivity of CF_3T makes it too difficult to handle in the large concentrations required. This problem does not occur in dissociation experiments because they are performed with much lower CF_3T concentrations that can be handled easily and safely.

The peak selectivities of T/H and T/D are several times higher at $5.2\text{ }\mu\text{m}$ than at $9.3\text{ }\mu\text{m}$, the wavelength that has been successfully employed for laser separation of T from H. Thus laser separation of T from H may be more economical at $5.2\text{ }\mu\text{m}$ than at $9.3\text{ }\mu\text{m}$. Furthermore, laser separation of T from D may become economical at $5.2\text{ }\mu\text{m}$, whereas it is not economical at $9.3\text{ }\mu\text{m}$. Therefore, experiments on multiphoton dissociation of CF_3T at $5.2\text{ }\mu\text{m}$ are warranted by the observed selectivities. The presentation concluded with a calculation of energy costs comparing dissociation at $5.2\text{ }\mu\text{m}$ and $9.3\text{ }\mu\text{m}$. The analysis demonstrates that dissociation at $5.2\text{ }\mu\text{m}$ is economically reasonable if the physics is similar to that at $9.3\text{ }\mu\text{m}$.

FUTURE WORK

Although dissociation experiments are desirable and necessary, they are not practical at the moment because there is not enough laser energy per pulse at $5.2\text{ }\mu\text{m}$ to conduct the simplest experiment in a reasonable time. Our best estimate of the least time required is 24 work weeks (7 hours a day, 5 days a week) of repetitive firing of the laser to dissociate only 10% of the CF_3T molecules in one gas mixture at one pressure. The problem stems from the large sample size required to count reliably a change in the numbers of CF_3T molecules. Two solutions to this problem are being investigated. The more direct solution is to increase the energy per pulse by employing a more efficient frequency-doubling crystal. Such crystals are being used in at least two major research labs in the United States, and we are actively pursuing the possibility of borrowing or purchasing one crystal. The second solution involves a technique for counting CF_3T molecules that will work on much smaller samples than are presently required. Some possible methods exist but they are much more time consuming and more costly than the present technique. Provided that this

problem is solved by one or both solutions then dissociation experiments will proceed. The results of these experiments will aid us in producing a reliable model of the laser isotope separation process and thus to calculate the design parameters of practical tritium separation plants.

CONCLUSIONS

The poster presentation at the Conference on Lasers and Electro-Optics was successful in that it generated ten requests for preprints (Appendix A). Thus there is still enthusiasm in the world scientific community for infrared multiphoton dissociation as a technique for separating tritium from protium and deuterium. Several new contacts were made in the course of the presentation and throughout the conference and these contacts may in turn prove helpful for our research at Ontario Hydro.

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REFERENCE

1. Morrison, H.D. and O'Neill, J.A. Trip Report: Conference on Lasers and Electro-Optics, May 21-24, 1985. Research Report 85-222-K.

APPENDIX A

ABSORPTION SELECTIVITY OF TRITIATED TRIFLUOROMETHANE AT 5 μm

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INTRODUCTION

Trifluoromethane (CF_3H) has been selected at Ontario Hydro as the process molecule for laser isotope separation of tritium from both protium and deuterium. Previous studies show that infrared multiphoton dissociation of trifluoromethane has only one decay channel and the products are easily separated /1/. Multiphoton dissociation of CF_3T has been demonstrated using CO_2 lasers at a wavelength of 9.3 μm /2,3/, but is only practical for T/H separation and not for T/D separation because of the low absorption selectivity for T/D. Separation of T from D by multiphoton dissociation of trifluoromethane requires a high absorption selectivity at another wavelength that is accessible by a high-power laser. CF_3T has a strong absorption band at 5.2 μm , a wavelength generated by frequency-doubled CO_2 lasers. This paper examines the optical absorption selectivity of CF_3T near 5.2 μm as a first step to assess the potential for multiphoton dissociation in this region. If selective dissociation does prove practical at 5.2 μm then it may be the only wavelength required for laser separation of tritium from both protium and deuterium.

APPENDIX A (cont'd)

EXPERIMENTAL APPARATUS AND TECHNIQUE

Figure 1 is a schematic diagram of the apparatus used for measuring the small-signal absorption spectrum of trifluoromethane in the wavelength region near 5.2 μm . The source for these measurements was a frequency-doubled grating-tunable CO_2 laser. The laser output consisted of a single-mode pulse on one of many lines in the P and R branches of the 10- μm band and with an energy up to 100 mJ. A spectrometer was used to verify the wavelength setting of the CO_2 laser. A laser pulse at 10 μm was partially converted to 5 μm by passing it through a properly oriented frequency-doubling crystal of tellurium. This method produces a pulse at a wavelength that is exactly half that of the incident 10- μm pulse. The 5- μm source was completed by a sapphire window that acted as a filter by absorbing the remaining 10- μm energy completely and transmitting more than half of the 5- μm energy. An energy conversion efficiency as high as 1.5% was obtained, and pulse energies at 5 μm exceeded 1 mJ for most of the lines.

Absorption in two isotopic forms of trifluoromethane gas, CF_3H and CF_3D , was examined as a function of gas pressure and wavelength. The gas was contained in a cell that consisted of a glass tube, 15 mm inner diameter and 88 cm long, sealed at both ends by NaCl windows at Brewster's angle. A single connection at one end of the cell allowed for gas filling and evacuation and for pressure monitoring by capacitance manometers. Absorption measurements were performed by splitting the collimated 5- μm beam in two parts to monitor simultaneously the energy before and after the gas cell. Thus the cell transmission was determined for each pulse by the ratio of the energies in the two beams. This two-beam technique greatly reduced the uncertainty in the signal due to variations in the pulse energy

APPENDIX A (cont'd)

from shot to shot. Further noise reduction was provided by averaging the signal over ten pulses for each absorption measurement. By this method an absorption as low as 0.5% could be detected.

RESULTS AND DISCUSSION

The absorption in CF_3H and CF_3D was measured for each CO_2 line as a function of pressure from 10 to 800 torr. Figure 2 displays the results of three runs on CF_3H at one frequency. The straight line is a least-squares fit to the data. The linear dependence of the absorption coefficient with pressure is typical of all the measurements. Thus the absorption at any frequency can be characterized by a single number given by the slope of the best-fit line to the pressure dependent absorption and designated as the absorption cross-section. Figures 3 and 4 show the absorption coefficient of pure CF_3H and CF_3D respectively as a function of frequency. (Note that $5.2 \mu\text{m}$ is equivalent to 1923 cm^{-1} .) The shaded regions in these figures indicate the frequencies that were not accessible. The cross-sections have been calculated for pure CF_3H and CF_3D by correcting the values measured in the experiment for the abundance of the other form. The samples of CF_3H contained 148 ppm CF_3D , and the CF_3D samples contained 2% CF_3H by volume.

The spectra of CF_3H and CF_3D in the $5\text{-}\mu\text{m}$ region have been recorded previously /4/ but this is the first quantitative report of accurate cross-sections. The cross-sections for CF_3T are also required to calculate the optical selectivity for tritium separation. Optical selectivity is defined as the ratio of absorption cross-sections of the appropriate isotopic molecules. A low resolution spectrum of CF_3T has been reported by Herman and Marling with sufficient information to calculate reliable cross-

APPENDIX A (cont'd)

sections /5/. The high specific activity of CF_3T makes it difficult to handle the concentration necessary to measure the absorption spectrum in our laboratory. The arrows in Fig. 3 and Fig. 4 indicate the positions of the R, Q and P branch peaks in the ν_1 fundamental band of CF_3T and corresponds to the C-T stretch vibration in the molecule. The labels accompanying the arrows identify the CO_2 laser lines that generate those frequencies.

The table in Fig. 5 lists the cross-sections of CF_3T and the optical selectivity for T/H and T/D separation in the three branches of the C-T vibration. In light molecules, such as trifluoromethane, the economics of laser tritium separation are dominated by the optical selectivity and only begins to be attractive where the selectivity is greater than 100. Separation of T from H has already been demonstrated at $9.3\text{ }\mu\text{m}$ using CO_2 laser energy directly /2,3/. At this wavelength T/H selectivity is 700 and the T/D selectivity is only 30. Figure 5 shows that in the $5.2\text{-}\mu\text{m}$ band the peak T/H selectivity is 5020, over 7 times greater than at $9.3\text{ }\mu\text{m}$, and the peak T/D selectivity exceeds 100. Thus, it is possible that laser isotope separation at $5.2\text{ }\mu\text{m}$ based on trifluoromethane will provide a single source method for removal of tritium from any mixture of hydrogen isotopes. However, before this prospect can be realized, multiphoton dissociation of CF_3T at $5.2\text{ }\mu\text{m}$ must be demonstrated. This requires a laser source with greater energy per pulse -- a minimum of 10 mJ. Energies of this order are possible by employing frequency doubling crystals with much higher conversion efficiencies and higher damage thresholds than those of tellurium. Recently such crystals have been developed elsewhere and two of these are CdGeAs_2 and AgGaSe_2 .

APPENDIX A (cont'd)

Experiments with higher energy pulses are required to establish the threshold energy fluence for dissociation. This parameter is crucial for developing an economic analysis of the laser isotope separation process. An example of such an analysis is illustrated in Fig. 6 that displays the photon energy cost per dissociation of one molecule of CF_3T at two wavelengths as a function of the laser pulse energy. The calculation assumes the removal of 1 ppm CF_3T from 50 torr of CF_3H , a dissociation threshold of 65 J/cm^2 at both wavelengths and a dielectric breakdown threshold of 100 J/cm^2 . A waveguide cell geometry was assumed for the calculation because it is known to be superior to conventional dissociation cell geometry; in all other respects the calculation is identical to that reported previously by O'Neill /3/. Although Fig. 6 appears to show that dissociation at $5.1 \mu\text{m}$ (using the 10R(22) line of CO_2) is more efficient than at $9.3 \mu\text{m}$, the displayed results do not account for the difference in photon energy or for the conversion efficiency of $5\text{-}\mu\text{m}$ photons from $10\text{-}\mu\text{m}$ photons. When these effects are properly considered dissociation at $5.1 \mu\text{m}$ is still more efficient than at $9.3 \mu\text{m}$ for conversion efficiencies greater than 10%. Obviously the calculations will change after the dissociation threshold is experimentally determined, but at least this simple analysis demonstrates that dissociation in the $5\text{-}\mu\text{m}$ region is economically reasonable if the physics is similar to that at $9.3 \mu\text{m}$.

Two other factors favour laser tritium separation in the $5.2\text{-}\mu\text{m}$ band. The peaks that appear in the spectra of CF_3H and CF_3D are due to combination bands and overtone vibrations. Thus by reducing the temperature of the gas the cross-sections of these molecules will decrease faster than the cross-sections of CF_3T and enhance the selectivity. The other factor

APPENDIX A (cont'd)

concerns the problem of frequency shifts due to replacement of carbon-12 by carbon-13 which occurs in natural abundance of 1.1%. These shifts complicate the absorption spectrum of trifluoromethane and reduce the selectivity for tritium /5/. At 9.3 μm the carbon isotope frequency shift is comparable to the hydrogen isotope frequency shift, while at 5.2 μm the carbon shift is much less than the hydrogen shift. Hence, carbon isotope shifts will not reduce the tritium selectivity at 5.2 μm as much as they do at 9.3 μm .

CONCLUSIONS

This paper describes detailed small-signal absorption measurements of CF_3H and CF_3D in the 5- μm region obtained by employing a frequency-doubled CO_2 laser. The experimental results demonstrate that the absorption is a linear function of pressure over a wide range and thus can be defined by a single cross-section for each wavelength. From known values of absorption in CF_3T the optical selectivity, defined as the ratio of cross-sections, was evaluated for T/H and T/D. The peak selectivities at 5.2 μm , 5020 for T/H and 145 for T/D, are several times higher than at 9.3 μm , the wavelength used in previous studies of multiphoton dissociation of trifluoromethane for tritium separation. In particular, the T/D selectivity is greater than 100, which implies that laser separation of tritium from deuterium could be economically attractive at 5.2 μm , but definitely not at 9.3 μm where the T/D selectivity is only 30. Thus, dissociation experiments on CF_3T at 5.2 μm are warranted by the measured selectivities and will be the next step in our research program.

APPENDIX A (cont'd)

REFERENCES

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2. Y. Makide, S. Hagiwara, T. Tominaga, K. Takeuchi and R. Nakane, Chem. Phys. Lett. 82, 18(1981).
3. J.A. O'Neill, Conference on Lasers and Electro-Optics Technical Digest, Paper TH121, 168(1984).
4. A. Ruoff, H. Bürger and S. Biedermann, Spectrochim. Acta 27A, 1359(1971).
5. I.P. Herman and J.B. Marling, J. Phys. Chem. 85, 493(1980).

FIGURE CAPTIONS

- Fig. 1: Schematic diagram of the experimental apparatus for measuring small-signal absorption of trifluoromethane in the 5- μ m wavelength region.
- Fig. 2: Experimental measurements of the absorption coefficient of CF₃H at 1935 cm⁻¹ as a function of pressure. The slope of the best-fit line yields the absorption cross-section.
- Fig. 3: Experimental measurements of the absorption cross-section as a function of frequency for CF₃H. The shaded area indicates the frequencies not generated by the frequency-doubled CO₂ laser.
- Fig. 4: Experimental measurements of the absorption cross-section as a function of frequency for CF₃D as in Fig. 3.
- Fig. 5: Table of optical selectivity for tritium from protium and deuterium at 5 μ m.
- Fig. 6: Calculated number of photons per dissociated molecule of CF₃T in a waveguide cell as a function of laser pulse energy at two wavelengths. The calculation assumes a gas mixture of 1 ppm CF₃T in 50 torr of CF₃H and a dissociation threshold fluence of 65 J/cm².

FIGURE 1

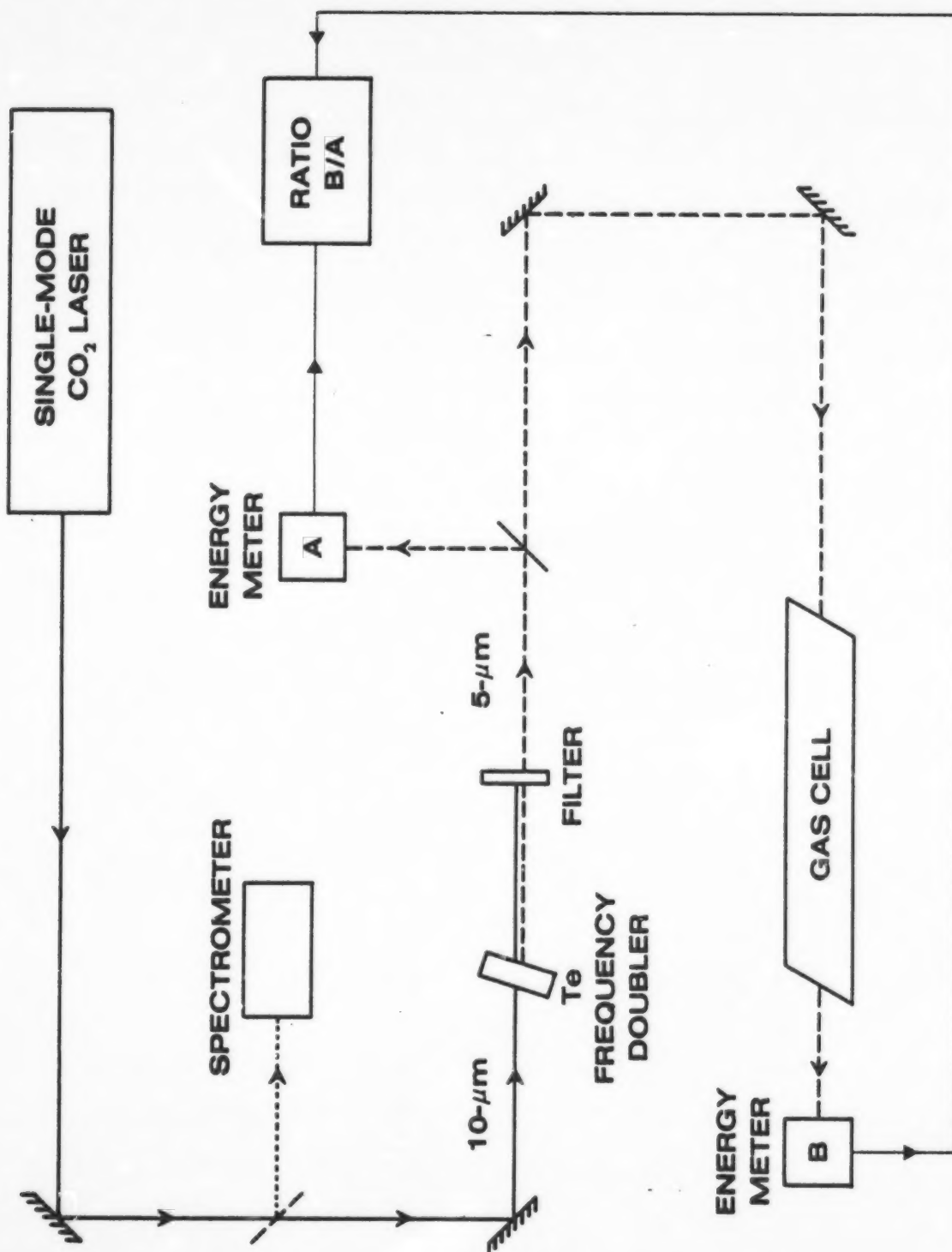


FIGURE 2

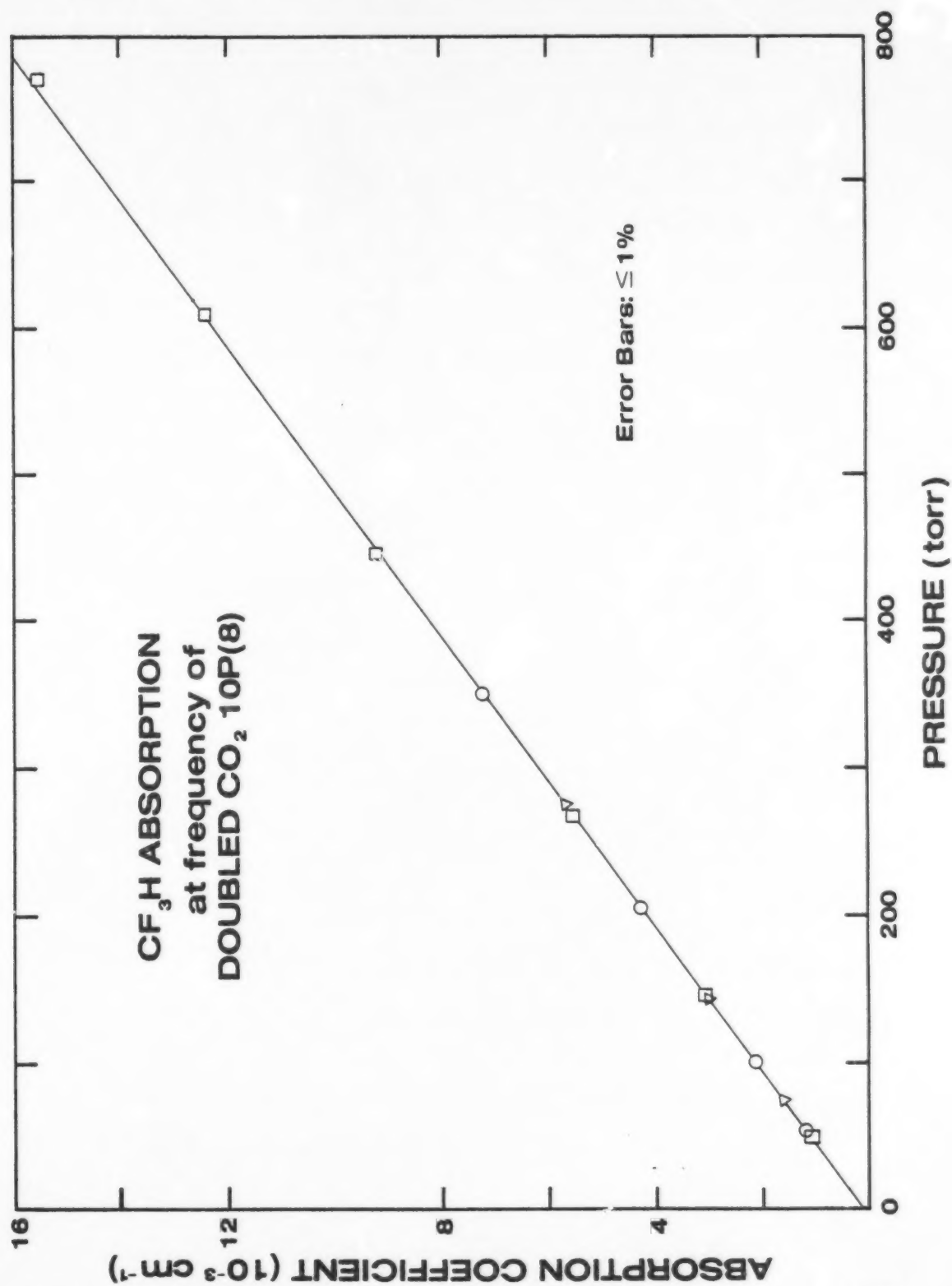


FIGURE 3

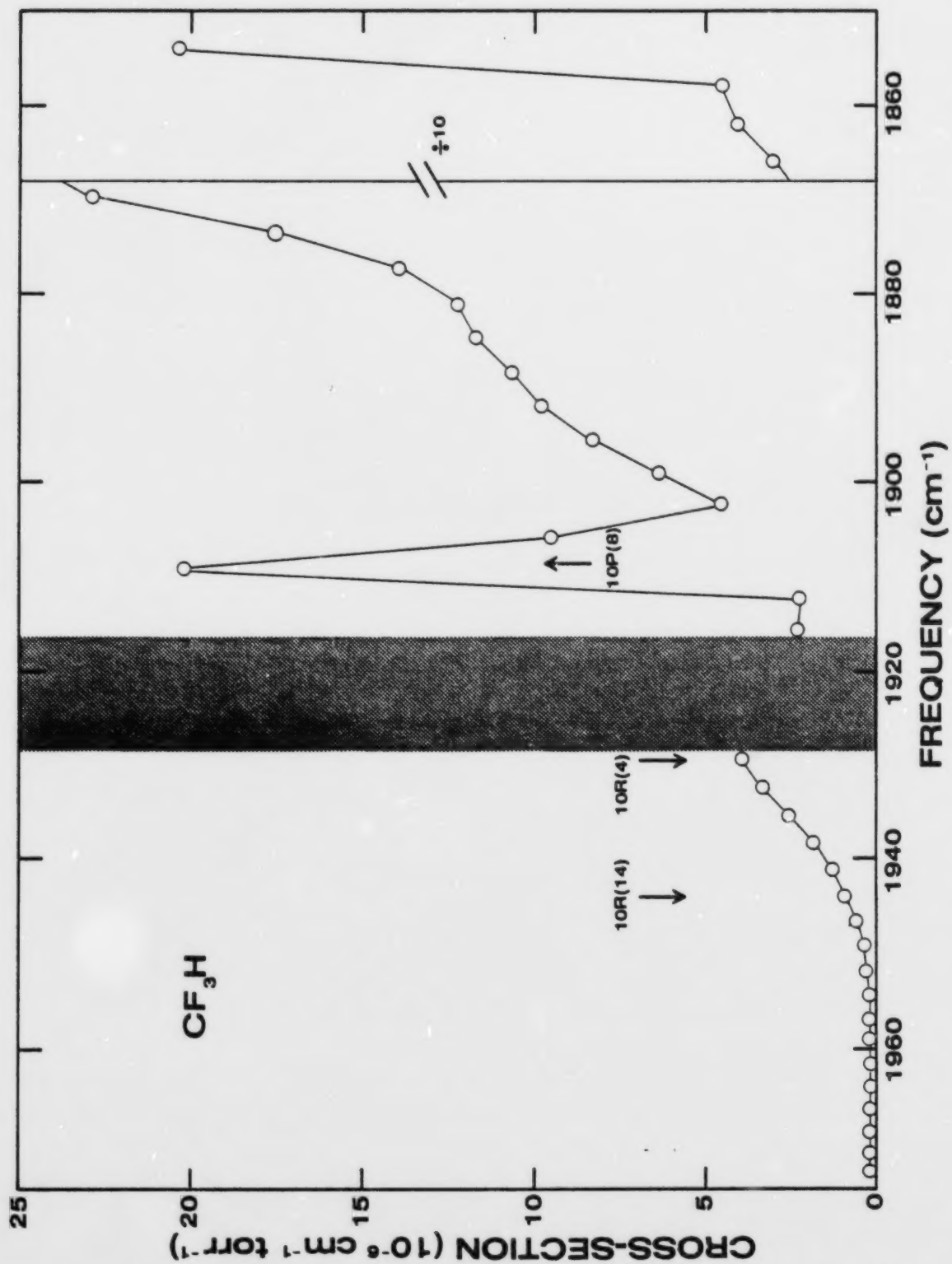


FIGURE 4

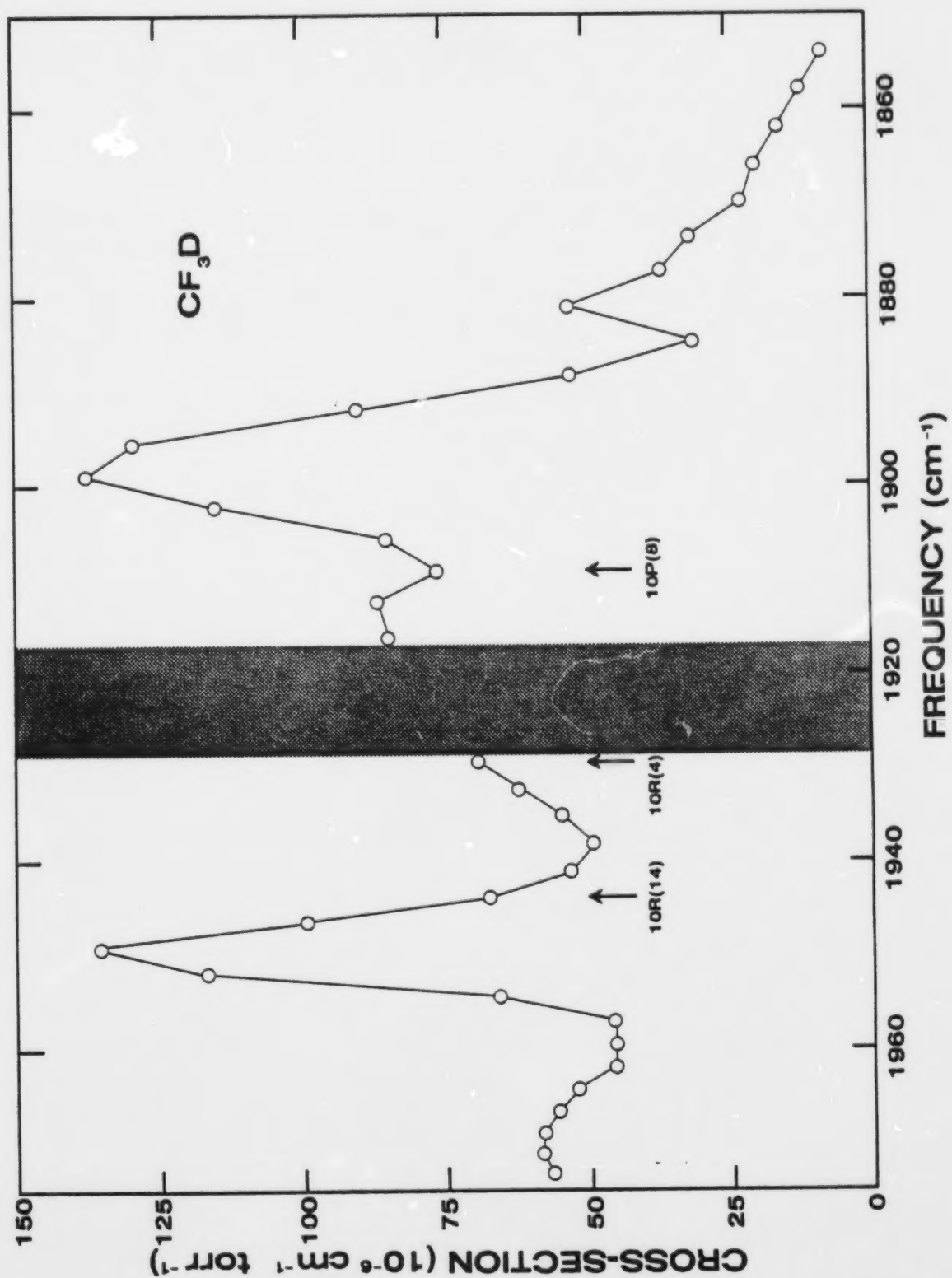


FIGURE 5

OPTICAL SELECTIVITY AT 5 μm

CO ₂ LINE	DOUBLED FREQUENCY [cm ⁻¹]	CF ₃ T* CROSS-SECTION [10 ⁻³ (cm.torr) ⁻¹]	SELECTIVITY	
			T/H	T/D
10P(14)	1899.0	1.2	189	9
10P(8)	1909.1	2.4	119	32
10R(4)	1929.5	10	2550	145
10R(8)	1935.4	1.0	390	18
10R(14)	1943.9	2.0	2200	30
10R(22)	1954.4	1.0	5020	15

*Estimated from I.P. Herman and J.B. Marling,
J.Phys. Chem. 85, 493-496(1981).

FIGURE 6

